

PATENT SPECIFICATION

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(54) PIGMENT-FREE COATING COMPOSITIONS

(71) We, DOW CORNING CORPORATION, of Midland, Michigan, United States of America, a corporation organized under the laws of the State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a protective coating composition. In one aspect, the invention relates to a transparent abrasion resistant coating. In another aspect, the invention relates to a stable dispersion of colloidal silica and a silicone resin.

There is a need for transparent glazing materials which exhibit a greater resistance to shattering than glass. Synthetic organic polymers can be formed into transparent enclosures and these materials, such as polycarbonates and acrylics, are finding use in glazing for autos, buses and aircraft and as windows in public buildings. While these polymers are easily fabricated into the desired shape, and are less dense and have more resistance to breakage than glass, their abrasion resistance is relatively low. This lack of surface hardness and abrasion resistance has severely restricted the use of these transparent polymeric materials. Other uses of the polymeric materials, such as glazing decorative architectural panels and mirrors, are also limited because of this lack of abrasion resistance.

Scratch resistant coatings, such as silica-containing solutions and polysilicic acid fluorinated copolymer compositions, are available in the prior art. These materials have found only limited commercial use because they are difficult to apply, poor in humidity resistance, or expensive. The coating composition of the present invention is based on relatively inexpensive commercially available materials which are easily applied to substrates to provide an abrasion resistant surface having

good weathering characteristics.

It is an object of the present invention to provide a composition suitable as a protective coating for solid substrates. It is another object of the invention to provide an improved abrasion resistant coating for solid substrates, especially transparent substrates. It is a further object of the invention to provide dispersions from which the coatings of the invention can be applied. These and other objects of the invention will be apparent to one skilled in the art upon consideration of the following description and appended claims.

In accordance with the present invention, there is provided an unpigmented aqueous coating composition comprising a dispersion of colloidal silica in a C₁—C₈ aliphatic alcohol-water solution of the partial condensate of a silanol of the formula RSi(OH)₂ in which R is selected from alkyl radicals of 1 to 3 inclusive carbon atoms, the vinyl radical, the 3,3,3-trifluoropropyl radical, the gamma-glycidyloxypropyl radical and the gamma-methacryloyloxypropyl radical, at least 70 weight percent of the silanol being CH₃Si(OH)₂, said composition containing 10 to 50 weight percent solids, said solids consisting essentially of 10 to 70 weight percent colloidal silica and 30 to 90 weight percent of the partial condensate, said composition containing sufficient acid to provide a pH in the range of 3.0 to 6.0.

As described above, the non-volatile solids portion of the coating composition is a mixture of colloidal silica and the partial condensate of a silanol. The major portion of the partial condensate, or silanol, is obtained from the condensation of CH₃Si(OH)₂; a minor portion, if desired, being obtained from cocondensation with C₂H₅Si(OH)₂,



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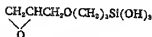
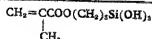
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or mixtures thereof. From both the standpoint of economy and optimum properties in the cured coating, it is preferred to employ monomethyltrisilanol in formulating the composition. When the partial condensate is of $\text{CH}_3\text{Si}(\text{OH})_3$, it is preferred that it be present in an amount in the range of from 40 to 60 weight percent of the total solids.

As will be described in detail in the examples, the trisilanols may be generated *in situ* by adding the corresponding trialkoxysilanes to acidic aqueous dispersions of colloidal silica. Suitable trialkoxysilanes are those containing methoxy, ethoxy, isopropoxy and *t*-butoxy substituents, which upon hydrolysis liberate the corresponding alcohol; thus, generating at least a portion of the alcohol present in the coating composition. Upon generation of the silanol in the acidic aqueous medium, there is condensation of the hydroxyl substituents to form $-\text{Si}-\text{O}-\text{Si}$ bonding. The condensation is not complete, but rather the siloxane retains an appreciable quantity of silicon-bonded hydroxyl groups, thus rendering the polymer soluble in the water-alcohol solvent. This soluble partial condensate can be characterized as a siloxanol polymer generally having at least one silicon-bonded hydroxyl group per every three $-\text{SiO}-$ units. During curing of the coating on a substrate, these residual hydroxyls condense to give a silsesquioxane, $\text{RSiO}_{1.5}$.

The silica component of the composition is present as colloidal silica. Aqueous colloidal silica dispersions generally have a particle size in the range of 5 to 150 millimicrons in diameter. These silica dispersions are prepared by methods well known in the art and are commercially available. It is preferred to use colloidal silica of 10 to 30 millimicron particle size in order to obtain dispersions having a greater stability and to provide coatings having superior optical properties. Colloidal silicas of this type are relatively free of Na_2O and other alkali metal oxides, generally containing less than 2 weight percent, preferably less than 1 weight percent Na_2O . They are available as both acidic and basic hydrosols. Colloidal silica is distinguished from other water dispersible forms of SiO_2 , such as nonparticulate polysilicic acid or alkali metal silicate solutions, which are not operative in the practice of the present invention.

The silica is dispersed in a solution of the siloxanol carried in a lower (C_1-C_6) aliphatic alcohol-water cosolvent. Suitable C_1-C_6 aliphatic alcohols include methanol,

ethanol, isopropanol and *t*-butyl alcohol. Mixtures of such alcohols can be used. Isopropanol is the preferred alcohol and when mixtures of alcohols are utilized it is preferred to utilize at least 50 weight percent of isopropanol in the mixture to obtain optimum adhesion of the coating. The solvent system should preferably contain from about 20 to 75 weight percent alcohol to ensure solubility of the siloxanol. Optionally, one can utilize an additional water-miscible polar solvent other than the C_1-C_6 alcohol, such as acetone and 2-butoxy ethanol in a minor amount, for example, no more than 20 weight percent of the cosolvent system.

To obtain optimum properties in the coating and to prevent immediate gelation of the coating composition, sufficient acid to provide a pH of from 3.0 to 6.0 must be present. Suitable acids include both organic and inorganic acids such as hydrochloric, acetic, chloroacetic, citric, benzoic, dimethylmalonic, formic, glutamic, glycolic, maleic, malonic, toluene-sulfonic and oxalic acids. The specific acid utilized has a direct effect on the rate of silanol condensation which in turn determines shelf life of the composition. The stronger acids, such as hydrochloric and toluene sulfonic acid, give appreciably shortened shelf or bath life and require less aging to obtain the described soluble partial condensate. It is preferred to add sufficient water-miscible carboxylic acid selected from acetic, formic, propionic and malic acids to provide a pH in the range of 4 to 5.5 in the coating composition. In addition to providing good bath life, the alkali metal salts of these acids are soluble, thus allowing the use of these acids with silicas containing a substantial (greater than 0.2% by weight Na_2O) amount of alkali metal oxide.

The coating compositions may be easily prepared by adding trialkoxysilanes, such as $\text{RSi}(\text{OC}_2\text{H}_5)_3$, to colloidal silica hydrosols and adjusting the pH to the desired level by addition of the organic acid. The acid can be added to either the silane or the hydrosol prior to mixing the two components provided that the mixing is done rapidly. The amount of acid necessary to obtain the desired pH will depend on the alkali metal content of the silica but is usually less than one weight percent of the composition. Alcohol is generated by hydrolysis of the alkoxy substituents of the silane, for example, hydrolysis of one mole of $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ generates 3 moles of ethanol. Depending upon the percent solids desired in the final composition, additional alcohol, water or a water-miscible polar solvent other than the aliphatic alcohol, can be added. The composition should be well mixed and allowed to age for a short period of time to ensure formation of the partial condensate. The coating composition thus obtained is a clear or slightly hazy low viscosity fluid which is stable for

several days. The condensation of SiOH continues at a very slow rate and the composition will eventually form gel structures. The bath life of the composition can be extended by maintaining the dispersion at below room temperature, for example, at 5°C .

Buffered latent condensation catalysts can be added to the composition so that milder curing conditions can be utilized to obtain the optimum abrasion resistance in the final coating. Alkali metal salts of the water-miscible organic acids, for example potassium formate, are one class of such latent catalysts: the sodium salts are particularly preferred. The amine carboxylates and quaternary ammonium carboxylates are another such class of latent catalysts. Of course, the catalysts must be soluble or at least miscible in the cosolvent system. The catalysts are latent to the extent that at room temperature they do not appreciably shorten the bath life of the composition, but upon heating the catalysts dissociate and generate a catalytic species active to promote condensation, for example, an amine. Buffered catalysts are used to avoid effects on the pH of the composition. Certain of the commercially available colloidal silica dispersions contain free alkali metal base which reacts with the organic acid during the adjustment of pH to generate the carboxylate catalysts *in situ*. This is particularly true when starting with a hydrosol having a pH of 8 or 9. The compositions can be catalyzed by addition of carboxylates such as dimethylamine acetate, ethanolamine acetate, dimethylamine formate, tetraethylammonium benzoate, sodium acetate, sodium propionate, sodium formate or benzyltrimethylammonium acetate. The amount of catalyst can be varied depending upon the desired curing condition, but at about 1.5 weight percent catalyst in the composition, the bath life is shortened and optical properties of the coating may be impaired. It is preferred to utilize from about 0.05 to 1 weight percent of the catalyst.

To provide the greatest stability in the dispersion form while obtaining optimum properties in the cured coating, it is preferred to utilize a coating composition having a pH in the range of 4 to 5 which contains 10 to 25 weight percent solids; the silica portion having a particle size in the range of 5 to 30 millimicrons; the partial condensate of $\text{CH}_3\text{Si}(\text{OH})_3$ being present in an amount in the range of 35 to 55 weight percent of the total solids in a cosolvent of methanol, isopropanol and water, the alcohols representing from 30 to 60 weight percent of the cosolvent and a catalyst selected from sodium acetate and benzyltrimethylammonium acetate being present in an amount in the range of 0.05 to 0.5 weight percent of the composition. Such a composition is relatively stable, having a bath life of approximately one month, and,

when coated onto a substrate, can be cured in a relatively short time at temperatures in the range of 75 to 125°C . to provide a transparent abrasion resistant surface coating.

The coating compositions of the invention can be applied to solid substrates by conventional methods, such as flowing, spraying or dipping to form a continuous surface film. Although substrates of soft plastic sheet material show the greatest improvement upon application of the coating, the composition can be applied to other substrates, such as wood, metal, printed surfaces, leather, glass, ceramics and textiles. As noted above, the compositions are especially useful as coatings for dimensionally stable synthetic organic polymeric substrates in sheet or film form, such as acrylic polymers, for example, poly(methylmethacrylate), polyester, for example, poly(ethylene terephthalate), and polycarbonates, such as poly(diphenylpropane) carbonate and poly(diethylene glycol-bis-allyl) carbonate, polyamides, polyimides, copolymers of acrylonitrile-styrene, styrene-acrylonitrile-butadiene copolymers, polyvinyl chloride, polybutyrate and polyethylene. Transparent polymeric materials coated with these compositions are useful as flat or curved enclosures, such as windows, skylights and windshields, especially for transportation equipment. Plastic lenses, such as acrylic or polycarbonate ophthalmic lenses, can be coated with the compositions of the invention. In certain applications requiring high optical resolution, it may be desirable to filter the coating composition prior to applying it to the substrate. In other applications, such as corrosion-resistant coatings on metals, the slight haziness (less than 5%) obtained by the use of certain formulations, such as those containing citric acid and sodium citrate, is not detrimental and filtration is not necessary.

By choice of proper formulation, including solvent, application conditions and pretreatment (including the use of primers) of the substrate, the coatings can be adhered to substantially all solid surfaces. A hard solvent-resistant surface coating is obtained by removal of the solvent and volatile materials. The composition will air dry to a tack-free condition, but heating in the range of 50° to 150°C . is necessary to obtain condensation of residual silanols in the partial condensate. This final cure results in the formation of a silsesquioxane of the formula $\text{RSiO}_{1.5}$ and greatly enhances the abrasion resistance of the coating. The coating thickness can be varied by means of the particular application technique, but coatings of about 0.5 to 20 micron preferably 2 to 10 micron thickness are generally utilized. Especially thin coatings can be obtained by spin coating.

The following examples are illustrative and not to be construed as limiting of the inven-

tion delineated in the claims.

Example 1.

Glacial acetic acid (0.2 grams) was added to 200 grams of a commercially available aqueous dispersion of colloidal silica having an initial pH of 3.1 containing 34% by weight SiO_2 of approximately 15 millimicron particle size and having a Na_2O content of less than 0.01 weight percent. Methyltrimethoxysilane (138 grams) was added to the stirred acidified dispersion generating methanol and methyltri-silanol. After standing for about one hour, the pH of the composition stabilized at 4.5. Portions of the composition were mixed with ammonium hydroxide or glacial acetic acid to adjust the pH of individual samples to provide compositions ranging in pH from 3.7 to 5.6. These compositions were aged for 4 days to ensure formation of the partial condensate of $\text{CH}_3\text{Si}(\text{OH})_2$ in the silica methanol-water dispersion. The composition contained 40% by weight solids, half of which was SiO_2 and the other half siloxane calculated on the basis $\text{CH}_3\text{SiO}_{1.5}$ weight available in the cured composition.

Six grams of each composition were flow-coated onto biaxially oriented, stretched panels of poly(methylmethacrylate). The acrylic panels were $4'' \times 6'' \times 0.137''$ and had been previously cleaned with isopropanol. The coated panels were allowed to air dry for 1 1/2 hours at room temperature and then cured at 85°C . for 4 hours in a forced air oven.

Portions of the aged compositions were diluted to 25 weight percent solids by addition of isopropanol, coated onto acrylic panels and cured in the same manner. Other portions of the compositions were aged for a total of eight days, then coated onto acrylic panels and subjected to the same curing cycles.

The adhesion and abrasion resistance of all the coatings was determined. Adhesion, as measured by pulling adhesive tape from a 1/8" crosshatched grid of the coating, was excellent to good except for a partial failure noted in some of the 8-day coatings. Abrasion resistance was determined by subjecting the coatings to circular rubbing with No. 0000 steel wool for five revolutions at 25 p.s.i. loading. The increase of optical haze of the abraded area was then measured by means of a Gardner large area hazemeter. The abrasion resistance data for the coatings at various pH levels and days of aging are tabulated in Table I.

Uncoated panels of this same stretched acrylic sheet show an increase in percent haze of 32 to 35 percent when tested by this method. These data demonstrate the effect of pH, percent solids and aging. The compositions having a pH of 4.5 and 5.0 were stable for over 21 days and gave the best scratch resistance.

A portion of the composition having a pH

of 4.5 and diluted to 25% solids with isopropanol was catalyzed by the addition of 0.28 weight percent benzyltrimethylammonium acetate after five days aging. The catalyzed composition was flow coated onto transparent, glass-reinforced polyester panels which are commercially available as a glazing material for solar energy collectors. The coating was cured at 70°C . for six hours. Adhesion of the coating was excellent and there was a slight improvement in light transmission. Abrasion resistance of the coating was good. Based on testing of other substrates, it is anticipated that long term weathering tests will show substantial improvement in the weatherability of the panels.

Example 2.

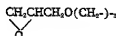
A coating composition containing 37 weight percent solids, 50% by weight of which were SiO_2 , was formulated by adding a basic colloidal dispersion of 13 to 14 millimicron silica (pH of 9.8, Na_2O content of 0.32% by weight) to methyltrimethoxysilane which had been acidified by the addition of 2.5 weight percent glacial acetic acid. After four hours mixing, the composition was divided into portions which were then adjusted to a pH of 3.9, 4.5 or 5.0 by addition of more glacial acetic acid. The compositions were then diluted to 25% solids by addition of isopropanol, aged for four days, coated onto acrylic panels, cured and tested in the manner described in Example 1. All panels showed no change in haze upon being abraded with the steel wool. This increase in hardness as compared to the coating of Example 1, especially that obtained from the composition at a pH of 3.7, is attributed to the catalytic action of sodium acetate which was formed upon addition of the colloidal silica to the acidified silane. The undiluted compositions (37% solids) were less stable and gelled within the four day aging period because of the presence of the catalyst.

A coating composition the same as described above having a pH of 4.5 and 25% solids was aged for 3 days and used to dip coat six spodumene ceramic heat exchanger core samples. The remaining coating composition was then diluted to 20% by weight with a 50/50 isopropanol-water cosolvent and used to dip coat six cordierite heat exchanger core samples having relatively small air passages. All coated specimens were cured at 100°C . for six hours. Three of each type of core were cured at 350°C . for an additional 20 hours. All of the coated cores exhibited improved strength and were more resistant to hot corrosive gases.

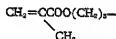
Example 3.

A number of coating compositions utilizing various trimethoxysilanes were prepared. The compositions were prepared by adding the

appropriate amount of silane to the aqueous colloidal silica dispersion described in Example 1 which had been acidified by the addition of 1 weight percent glacial acetic acid to a pH of about 4.5. The solids consisted of 50 weight percent SiO_2 and 50 weight percent of the partial condensate of $\text{RSi}(\text{OH})_2$, calculated as $\text{RSiO}_{1/2}$. After three days, the compositions were diluted to 20% solids with isopropanol. In the case of where $\text{R} = \text{CF}_3\text{CH}_2\text{CH}_2-$,

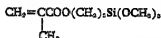


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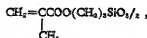
gellation occurred within this three day period. Fresh compositions were formulated and diluted to 20% solids with isopropanol after four hours and allowed to stand for two days.

The compositions were coated onto clean stretched acrylic panels, as previously described, allowed to air dry for 15 minutes and then cured for four hours at 85°C. The coated panels were tested for abrasion resistance by means of the described steel wool abrasion test. Results obtained by the use of the different silanes are tabulated in Table II. A mixture of silanes was then utilized in formulating the above type of composition. A mixture of 90 weight percent $\text{CH}_3\text{Si}(\text{OCH}_2)_2$ and 10 weight percent $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2)_2$ used in place of the monomethyltrimethoxysilane in the composition gave a coating exhibiting a delta haze of 2.0%. A similar coating formed from a mixture of 80% by weight $\text{CH}_3\text{Si}(\text{OCH}_2)_2$ and 20% by weight



had equivalent abrasion resistance.

These data demonstrate the necessity of using compositions containing a major amount of the partial condensate of $\text{CH}_3\text{Si}(\text{OH})_2$. Those cured coatings based on other silsesquioxanes, such as $\text{C}_6\text{H}_5\text{SiO}_{1/2}$ and



were softer than the acrylic surface itself.

Example 4.

Various amounts of methyltrimethoxysilane were added to an acidified aqueous colloidal

dispersion as described in Example 1 and the pH of the compositions was adjusted to 4.5. After four days, the compositions were diluted to 20% solids with isopropanol and flow coated onto acrylic panels, air dried and cured for two hours at 85°C. Abrasion resistance (percent delta haze from the steel wool test) of the different coatings is tabulated below:

Composition of Cured Coating (Solids Content)	% Change in Haze	
10% $\text{CH}_3\text{SiO}_{1/2}$		60
90% SiO_2	*	
20% $\text{CH}_3\text{SiO}_{1/2}$		
80% SiO_2	*	
30% $\text{CH}_3\text{SiO}_{1/2}$		65
70% SiO_2	1.0	
40% $\text{CH}_3\text{SiO}_{1/2}$	2.0	
60% SiO_2		
50% $\text{CH}_3\text{SiO}_{1/2}$	0.4	
50% SiO_2		70
*coating flaked off when cured.		

The data demonstrate that a minimum amount (at least 30 weight percent based on the solids content) of $\text{CH}_3\text{SiO}_{1/2}$ must be present in the coating.

Example 5.

Different amounts of sodium acetate were added to an acidified colloidal silica dispersion which was initially substantially free of alkali metal salts. Sufficient methyltrimethoxysilane was added to the dispersion to form a 50:50 SiO_2 : $\text{CH}_3\text{SiO}_{1/2}$ coating and the pH of each composition was adjusted to 4.5 by addition of glacial acetic acid. After one to four days, the compositions were diluted to 20 percent solids with isopropanol, coated onto acrylic panels and cured for four hours at 85°C. Abrasion resistance (percent delta haze by steel wool abrasion) is tabulated below:

Wt. % Sodium Acetate Present in Original Silica Dispersion	% Change in Haze Upon Abrasion	
0	1.0*	90
0.0625	0.3*	
0.125	0.3	95
0.25	0.5	
0.50	0.8	
1.0	0.3	
2.0	14.8	100
*coated after four days, all others coated after one day.		

Equivalent results (delta haze of less than 1 percent) were obtained when trimethylbenzyl ammonium acetate was used in amounts in the range of 0.05 to 0.25 weight percent of the composition. Following the above procedure,

the optimum amount of any of the latent catalysts described in the specification can be readily determined.

Example 6.

- 5 For purposes of comparison, ethylorthosilicate was utilized as the SiO_2 source as disclosed in U.S. 3,642,681. One hundred grams of ethylorthosilicate was hydrolyzed by addition to 47 grams of ethanol in 45 grams of 10 0.1N aqueous hydrochloric acid. After one hour sufficient amounts of various silanes were added to samples of the hydrolyzed ($\text{C}_2\text{H}_5\text{O}$) Si to form a composition in which 15 50% of the solids were SiO_2 . These solutions were diluted with isopropanol and acetic acid to give 10% solutions which would wet acrylic panels. After coating, the panels were heated at 85° C. for 16 hours to ensure complete cure. Abrasion resistance was determined by the previously described steel wool test. Results are tabulated below:

	Silane Added to the Ethylorthosilicate Solution	% Delta Haze
25	$\text{CH}_3\text{Si}(\text{OCH}_3)_3$ $\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$ $\text{CH}=\text{CCOO}(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_3$ CH_3	18.7 25.7 21.5

- These data demonstrate the inferior performance of silica solutions of hydrolyzed ethylorthosilicate when used in the aqueous coating compositions as above. The silica must be in the form of a colloidal dispersion in order to obtain superior abrasion resistance.

Example 7.

- 35 Methyltrimethoxysilane (50.0 grams) was acidified with 1.0 gram of acetic acid. A colloidal silica dispersion (66.7 grams) as described in Example 2 was added to the acidified silane to provide a methanol-water dispersion of silica and soluble partial condensate. The solids were 40% by weight SiO_2 and 60% by weight the partial condensate of $\text{CH}_3\text{Si}(\text{OH})(\text{OCH}_3)_2$, when calculated as CH_3SiO_2 . After diluting to 22.5% solids, with isopropanol, the pH of the composition was adjusted to 5.35. After five days, the composition was filtered and coated onto panels of poly(diethyleneglycolbisallyl)carbonate which had been treated by soaking overnight in a 10% 50 by weight solution of potassium hydroxide. The coating was cured at 100° C. for two hours.

- A second portion of the described coating composition was catalyzed by addition of 0.1 weight percent trimethylberzyl ammonium acetate, coated onto silvered acrylic panels (mirrors) and onto panels of polycarbonate, pretreated as described above. The catalyzed

coatings were cured at 85° C. for two hours.

The coated panels, both mirrored acrylic and polycarbonate, were tested by the circular steel wool rubbing method and showed a delta haze of less than 1%.

The coated polycarbonate panels were tested by the Taber Abrasion test method. The coatings were abraded until 10% haze was developed, the number of revolutions being reported as the multiple of the number of revolutions necessary to give this same amount of haze on uncoated acrylic panels. The data is set out in Table III.

As with poly(methylmethacrylate), the poly(diethyleneglycol bis allyl) carbonate is especially useful in molding ophthalmic lenses. After molding, such lenses can be coated with the compositions of the invention to provide an extended service life.

80 Panels of commercially available transparent polycarbonate were primed with a 5% by weight solution of a silane-modified epoxy resin in Dowanol—EM ("Dowanol" is a Registered Trade Mark) and allowed to air dry. The epoxy primer was a mixture of about 20% by weight beta-aminoethyl-gamma-aminopropyltrimethoxysilane in a commercially available liquid epoxy resin. The primed panels were coated with a composition the same as that described in Example 1 (pH=3.9) which was diluted to 25% solids with isopropanol and catalyzed by addition of 0.2 weight percent trimethylbenzyl ammonium acetate. The coating passed the cross-hatching tape adhesion test and the abrasion resistance was also excellent.

Other polymer substrates which benefit from use of the coating of the present invention include polyvinyl chloride, polystyrene, silicone resin and rubber, cellulosic thermoplastics and polyesters.

Example 8.

100 Methyltrimethoxysilane (75.7 parts by weight) which had been acidified with 18.9 parts by weight acetic acid was mixed with 126.1 parts by weight of the 50% solids precursor colloidal silica dispersion described in Example 1. There was a slight exotherm and the mixture was cooled. After five hours, another 8 parts by weight acetic acid was added to provide a pH of 4.5. After eleven hours, the composition was diluted by addition of 100 parts by weight isopropanol. The composition was then aged for 3 1/2 days and dip coated onto stretched acrylic panels. The coating was air dried and then cured for 4 hours at 85° C.

Coated panels were placed in a humidity test chamber maintained at 74° C. and 100% humidity. Other coated panels were exposed in a weatherometer under the conditions described in ASTM—G—25—70. For purposes of comparison, a commercially available acrylic sheet coated with a polysilicic acid/fluoro-

olefin-hydroxyalkyl vinyl ether copolymer was also tested. Results of the steel wool abrasion test (25 p.s.i.) after the indicated number of revolutions and exposure times are tabulated in Table IV. Another acrylic panel coated with the above-described composition of the invention was exposed for over 21 days in the weatherometer and was not visibly scratched by the steel wool at 25 p.s.i. loading after 5 revolutions.

Other acrylic panels coated and cured as described above were submitted to other testing to determine utility as enclosures (windshields) for transportation equipment. After a gauze pad soaked in the particular solvent was placed on the cured coating and covered with a watch glass for 24 hours at room temperature, there was no apparent effect from such contact with benzene, toluene, xylene, trichloroethane, acetone, ethyl acetate, butylamine, methanol, isopropanol, permanent antifreeze, gasoline or motor oil.

Another such coated acrylic panel was abraded with a windshield wiper blade loaded at 0.35 lbs./in. of length moving in an arc at 80 cycles per minute. A 15% by weight sodium chloride solution was sprayed on the test panel surface at 5-minute intervals. The test was terminated after 12,420 cycles and there was no visible effect on the arc surface area.

Thermal shock characteristics of the coating were determined by temperature cycling of a coated panel from -18°C. to 70°C. in about 20 minutes. After six cycles, the coating remained intact with no apparent effect on optical properties.

These data demonstrate that in addition to abrasion resistance the coatings of the invention possess excellent weathering characteristics, solvent resistance and thermal stability.

Example 9.

A coating composition similar to that described in Example 8 except that isopropanol was not present was sprayed onto clean aluminum panels. After air drying for 24 hours, the coated panels were tested in a Dew Cycle Weatherometer. After 100 hours of testing, the panels showed very low corrosion (2%) and there was no blistering in the coating. These data demonstrate the utility of the compositions as corrosion resistant coatings for metal.

Example 10.

The utility of various organic acids in formulating the compositions of the invention was demonstrated by diluting formic and maleic acid to 25% by weight solutions with a 50/50 isopropanol-water cosolvent. Oxalic acid was diluted to a 12.5% by weight solution with the same cosolvent. Each of the diluted acids was added to 10.0 gram portions of a 30% solids aqueous colloidal silica having

13 to 14 millimicron particles, a pH of 9.8 and Na_2O (titratable alkali) of 0.32% by weight. Sufficient acid was added to bring the pH down to the range 3.5 to 4.1. Methyltrimethoxysilane (6.0 grams) was added to each of the acidified silicas. After 30 minutes mixing, the compositions were reduced to 25% solids by the addition of isopropanol and aged for about 18 hours. The composition based on oxalic acid contained a small amount of precipitate which had settled out during aging. The aged compositions were flow coated onto glass microscope slides, air dried and then cured at 100°C. for 2 1/2 hours.

The clear cured coatings were tested for abrasion resistance by attempting to mar the surface with a pencil eraser. The abrasion resistance of the composition acidified with formic acid was excellent, while the coating based on maleic and oxalic acid exhibited very good abrasion resistance.

Example 11.

The procedure of Example 10 was repeated utilizing a 25% by weight solution of glycolic acid and a colloidal silica dispersion containing about 0.05% by weight Na_2O and having an initial pH of 3.1. After dilution to 25% solids with isopropanol, the pH was 3.6. After aging for about 4 hours, about 25 grams of the composition was catalyzed with 0.15 grams of a 10% by weight solution of benzyltrimethylammonium acetate raising the pH to 4.7. When coated onto a glass slide and cured, the clear coating had good to very good abrasion resistance when tested with an eraser.

The coating composition was then further catalyzed by the addition of 0.5 grams of 10% by weight isopropanol solution of triethylamine which elevated the pH to 5.2. The coating, cured onto glass slides, exhibited very good abrasion resistance but have a slight (about 3% haze) reduction in light transmission upon curing. This small amount of haze is not objectionable when the coating is used in the applications other than the optical area.

Example 12.

Three different aqueous colloidal silicas were blended to provide a 32% solids dispersion containing one-third of 50 to 70 millimicron-sized particles, one-third of 15 to 17 millimicron sized particles and one-third 6 to 7 millimicron sized particles having an Na_2O content of about 0.2 weight percent. Acetic acid (2.25 grams in 10 ml. of water) was added to 87.5 grams of the colloidal silica dispersion. After acidification, 45 grams of methyltrimethoxysilane was added rapidly and the mixture was shaken. After 45 minutes, hydrolysis was considered complete and 57.75 grams of isopropanol was added to provide a coating composition containing 25% solids (calculated on the weight of SiO_2 , plus

$\text{CH}_3\text{Si}(\text{OCH}_3)_2$) and having a pH of 5.4.

After two days aging, the solution/dispersion of colloidal silica and partial condensate was filtered and a portion was coated onto one-eighth inch thick stretched acrylic sheet. After air drying for 30 minutes, the coating was cured for four hours at 80° C.

- When tested for abrasion resistance with steel wool as described in Example 1, there was no apparent change in haze. The number of revolutions was increased to 25 but there was still no measurable abrasion. The loading was then increased from 25 p.s.i. to 35 p.s.i. and after 10 revolutions, there was no measurable increase in haze. The exceptional hardness of this coating is believed to result from the more dense packing of particles obtained by use of the blend of different particle sizes.

A second portion of the aged coating composition was flow-coated onto a 100 mil thick molding of a commercially available styrene-acrylonitrile copolymer which had been primed with the silane-modified epoxy resin described in Example 7. After air drying for 30 minutes, the coating was cured for six hours at 75° C.

The cured coating exhibited excellent abrasion resistance when subjected to the steel wool rubbing test. A portion of the coating was cross-hatched into 1/16 inch squares using a razor blade to cut through to the styrene-acrylonitrile substrate. The cross-hatched coating was not lifted by rapidly removing pressure-sensitive tape previously pressed onto the cut surface. These data demonstrate the abrasion resistance and adhesion obtained by the practice of the invention.

TABLE I

Abrasion Resistance - % Delta Haze

pH of Composition	3.7		4.5		5.0		5.6	
% Solids in Composition	40	25	40	25	40	25	40	25
% Delta Haze 4 day Composition	6	4	0.4	0.8	0.4	0.5	6	6
% Delta Haze 8 day Composition	6	4	6	2	2	2	5*	6

* small gel particles in sample

TABLE II

Silane Used In Coating Composition	Abrasion Resistance of Coating (% Change in Haze)
$\text{CH}_3\text{Si}(\text{OCH}_3)_2$	3.2
$\text{C}_2\text{H}_5\text{Si}(\text{OCH}_3)_2$	Composition gelled
$\text{CH}_3\text{-CHSi}(\text{OCH}_3)_2$	9.0
$\text{C}_4\text{H}_9\text{Si}(\text{OCH}_3)_2$	45.5
$\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_2$	33.5
$\text{CH}_3\text{-C}(\text{COO}(\text{CH}_3)_2)\text{Si}(\text{OCH}_3)_2$	50.7
$\text{CH}_3\text{-CH}(\text{CH}_3)\text{Si}(\text{OCH}_3)_2$	39.0

TABLE III

Panel	Taber Abrasion (X Acrylic)	
	Minimum Abraded Area	Maximum Abraded Area
Uncoated polycarbonate	24 X	24 X
40 SiO ₂ :60 CH ₃ SiO ₂ / ₂ uncatalyzed	580 X	375 X
40 SiO ₂ :60 CH ₃ SiO ₂ / ₁ catalyzed	670 X	350 X

TABLE IV

Exposure Conditions	Coating Material (solid content)	Abrasion Resistance (° Delta Haze) after			Appearance before Abrasion
		5 Rev.	10 Rev.	15 Rev.	
Initial (no exposure)	50% SiO ₂ , 50% CH ₃ SiO _{1/2}	0.7	0.8	1.0	good
	Polysilicic acid/fluoro copolymer	1.6	2.2	3.5	Excellent
120 Hrs. — Humidity Chamber	50% SiO ₂ , 50% CH ₃ SiO _{1/2}	0.2	0.2	1.9	good
	Polysilicic acid/fluoro copolymer	40.2	—	—	permanent water spots
240 Hrs. — Humidity Chamber	50% SiO ₂ , 50% CH ₃ SiO _{1/2}	0.6	1.4	5.6	good
	Polysilicic acid/fluoro copolymer	44.0	—	—	permanent water spots
7 Days — Weatherometer	50% SiO ₂ , 50% CH ₃ SiO _{1/2}	0.5	0.7	0.5	good
	Polysilicic Acid/fluoro copolymer	1.3	5.4	15.7	good

WHAT WE CLAIM IS:—

1. A pigment-free aqueous coating composition comprising a dispersion of colloidal silica in a C—C aliphatic alcohol-water solution of the partial condensate of a silanol of the formula RSi(OH)₃ in which R is selected from alkyl radicals of 1 to 3 inclusive carbon atoms, the vinyl radical, the 3,3,3-trifluoropropyl radical, the gamma-glycidioxypropyl radical and the gamma-methacryloxypropyl radical, at least 70 weight percent of the silanol being CH₃Si(OH)₃, said composition

containing 10 to 50 weight percent solids consisting essentially of 10 to 70 weight percent colloidal silica and 30 to 90 weight percent of the partial condensate, said composition containing sufficient acid to provide a pH in the range of 3.0 to 6.0.

2. A coating composition in accordance with claim 1 in which the alcohol in the alcohol-water solvent is present in an amount in the range of 20 to 35 weight percent based on the total weight of the solvent.

3. A composition in accordance with claim

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- 2 wherein at least 50 weight percent of the alcohol is isopropanol.
4. A composition in accordance with claim 2 wherein the alcohol-water cosolvent contains a water-miscible polar solvent other than the aliphatic alcohol, in an amount up to 20 weight percent based on the weight of cosolvent.
- 5 5. A composition in accordance with claim 4 wherein the polar solvent is acetone.
- 10 6. A composition in accordance with claim 2 wherein the acid is a water-miscible organic acid selected from acetic acid, formic acid, propanoic acid and maleic acid.
- 15 7. A composition in accordance with claim 6 containing from 0.05 to 1.5 weight percent of a buffered latent silanol condensation catalyst.
- 20 8. A composition in accordance with claim 7 containing as the catalyst, the sodium salt of the water miscible organic acid.
9. A composition in accordance with claim 7 containing as the catalyst a carboxylic acid salt of an amine.
10. A composition in accordance with claim 7 containing as the catalyst a quaternary ammonium carboxylate.
11. A composition in accordance with claim 10 wherein the catalyst is benzyltrimethyl ammonium acetate.
12. A composition in accordance with claim 6 wherein the partial condensate is of $\text{CH}_3\text{Si}(\text{OH})_2$.
13. A composition in accordance with claim 12 wherein the partial condensate is present in an amount in the range of from 40 to 60 weight percent of the total solids.
14. A composition in accordance with claim 13 wherein the $\text{C}_1\text{--C}_6$ aliphatic alcohol is a mixture of methanol and isopropanol.

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